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REVIEW

Redox processes in water remediation

Praveen Kumar Tandon[1] **· Santosh Bahadur Singh**[2]

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Abstract Groundwater is the main source of drinking water and water for agricultural and industrial usage. Therefore, groundwater contamination is prevented and contaminated groundwater is remediated to protect public health and the environment. Methods to remediate groundwater contamination have been recently developed. The use of redox processes in water remediation technologies has not been properly reviewed. Numerous water remediation technologies, such as ultrasonication, bioremediation, electrokinetics and nanotechnology, are closely related to redox processes. Redox processes control the chemical speciation, bioavailability, toxicity, mobility and adsorption of water pollutants in environment. Here, we review (1) general introduction of redox processes, (2) applicability of redox processes in water remediation, and (3) catalytic enhancement of redox potentials to explore its wide applicability in environmental remediation.

Keywords Water remediation · Redox processes · Ultrasonication · Toxicity · Environmental remediation

Introduction

Water remediation technologies include the processes that are mainly used to reduce and/or remove various pollutants from the contaminated water. Only 0.79 % of the total fresh water (i.e., 0.80 % of total water present on earth) resources present on the earth contribute to groundwater (Kotwicki 2009) that is the major and preferred source of drinking water in rural and urban areas, particularly in developing countries like India. Chemical composition is the prime factor on which suitability of water for domestic, industrial or agricultural purposes depends. Human activities, mainly responsible for depleting earth's natural resources, cause major disturbances in our environmental cycle which is based on redox processes. Disturbances in the environmental cycle have resulted in the increased level of pollutants in drinking water, air and soil, making life on earth more and more difficult day by day. In the present scenario, issues related to the remediation of environmental and groundwater pollution have attracted major attention of researchers due to their necessity for sustainability of life on the earth. The knowledge and study of redox processes may become a boon for refinement of water remediation technologies such as ultrasonication, bioremediation and nanotechnology. Redox processes typically involve the reduction/oxidation reactions that chemically convert the hazardous contaminants into nonhazardous or less toxic compounds that are more stable, less mobile or inert. This article is an abridged version of the chapter by Tandon and Singh (2015) published in the book series Environmental Chemistry for a Sustainable World (http://www.springer.com/series/11480).

Core concepts of redox processes

Redox (oxidation–reduction) reactions play very important role in our life. Generation of heat, electricity, energy or reactions occurring in electrochemical cells is a class of redox reactions. Conversion of hazardous contaminants into nonhazardous compounds and the reactions occurring

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✉ Praveen Kumar Tandon
pktandon1@gmail.com

[1] Department of Chemistry, University of Allahabad, Allahabad, Uttar Pradesh 211002, India

[2] Department of Chemistry, National Institute of Technology, Raipur, Chhattisgarh 492010, India

in living organisms are one or the other form of redox processes. Commonly used oxidants in water remediation are hexacyanoferrate(III), ferrate(VI), ozone, hydrogen peroxide, hypochlorites, chlorine, chlorine dioxide, potassium permanganate and Fenton's reagent (hydrogen peroxide and iron) (US EPA 2011). Similarly, most commonly used reductants in water treatment are Fe^{2+}, Fe^0, calcium polysulfide, sodium dithionite, etc.

The principal forms of arsenic in natural waters are arsenate [As(V)] and arsenite [As(III)]. Arsenate exists as oxyanions ($H_2AsO_4^{1-}$ or $HAsO_4^{2-}$) in a pH range of 2–12, while arsenite remains as neutral undissociated species (H_3AsO_3) below a pH of 9.2 (Manning et al. 2002; Kanel et al. 2006). Arsenite ion can exhibit various degrees of protonation depending on the pH of the solution (Mohan and Pittman 2007).

$$AsO_3^{3-} + H^+ \xrightleftharpoons{pKa=13.40} HAsO_3^{2-} \tag{1}$$

$$HAsO_3^{2-} + H^+ \xrightleftharpoons{pKa=12.13} H_2AsO_3^{-} \tag{2}$$

$$H_2AsO_3^{-} + H^+ \xrightleftharpoons{pKa=9.22} H_3AsO_3 \tag{3}$$

Degree of protonation of As(III) and As(V) species is the governing factor to predict mobility of these species. In the range of pH (between 6 and 8) of groundwater, As(III) species is neutral, while As(V) is negatively charged. Mobility of negatively charged As(V) decreases due to electrostatic forces of attraction arising due to the presence of positively charged particles in system.

Redox processes and its environmental concern

All processes of life on earth utilize energy derived from the redox processes. Transformation of matter from one form to another form includes a number of cycles of various elements, and life is directly related to the electron transfer (redox) reactions. Example includes the cycles of carbon (C), nitrogen (N), sulfur (S), iron (Fe) and manganese (Mn), as well as those of redox-sensitive trace elements such as arsenic (As), chromium (Cr), copper (Cu) and uranium (U). The chemical speciation, bioavailability, toxicity and mobility of these elements in the environment are directly affected by redox processes that occur in the environment (Borch et al. 2010). Understanding of aqueous redox processes can provide new opportunities to develop or engineer new strategies for water remediation and is also very important for predicting and protecting environmental health. Environmental redox processes play key roles in the formation and dissolution of mineral phases and control the chemical speciation, bioavailability, toxicity and mobility of many major and trace elements. Redox-active humic substances and mineral surfaces can catalyze the redox transformation and degradation of organic contaminants (Borch and Fendorf 2008; Moberly et al. 2009). Microorganisms coupled to the electron acceptors can release and store energy via oxidation of labile organic or inorganic compounds (electron donors). Environmental mobility of potentially hazardous metals, such as Cd, Ni and Zn is indirectly related to redox conditions because these metals form ionic complexes and solid precipitates with redox-sensitive elements. Redox conditions regulate many of the biogeochemical reactions in the soil system. However, in order to achieve these conditions, a number of factors must be simultaneously fulfilled in soil system (Trolard and Bourrie 2008). Schematic representation of the importance of redox processes and its related environmental issues is given in Fig. 1.

Remediation technologies based on redox processes focus on modifying the chemistry and microbiology of water by injecting selected reagents into the contaminated water to enhance the degradation and extraction of various contaminants by in situ chemical oxidation/reduction reactions (Yeung 2009). Thus, redox process-mediated remediation technologies are applicable for the remediation of a wide range of inorganic, organic, and mixed water contaminants.

Oxidation and water remediation

Oxidation is a promising technology to remediate wastewater contaminated by heavy metals, inorganic, organic and other contaminants. However, oxidation alone does not remove contaminants from water itself and must be coupled with other remediation processes such as coagulation, adsorption or ion exchange, and filtration. Oxidants such as FeO_4^{2-}, H_2O_2, $K_3Fe(CN)_6$, O_3, Cl_2, HClO and ClO_2 are widely used for oxidation/disinfection and removing the organic materials that are resistant to

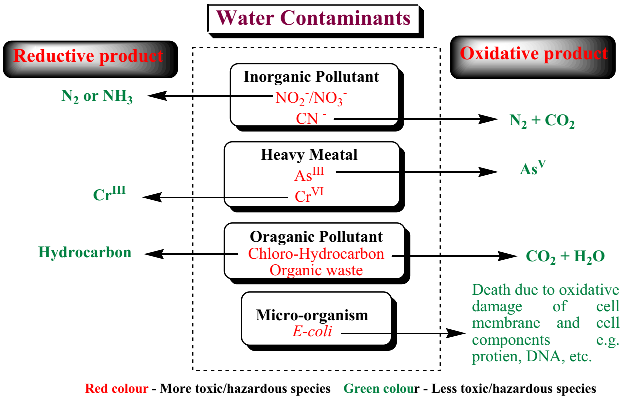


Fig. 1 Water contaminants and redox processes

Table 1 Oxidants/disinfectants used in water remediation and their redox potentials

Oxidants	Reactions	pH	E° (V)
Iron(VI)	$FeO_4^{2-} + 8H^+ + 3e^- \rightleftharpoons Fe^{3+} + 4H_2O$	Acidic	+2.20
	$FeO_4^{2-} + 4H_2O + 3e^- \rightleftharpoons Fe(OH)_3 + 5OH^-$	Basic	+0.72
Hydrogen peroxide	$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	Acidic	+1.78
	$H_2O_2 + 2e^- \rightleftharpoons 2OH^-$	Basic	+0.88
Potassium permanganate	$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O$	Acidic	+1.68
	$MnO_4^- + 2H_2O + 3e^- \rightleftharpoons MnO_2 + 4OH^-$	Basic	+0.59
Ozone	$O_3 + 2H^+ + 2e^- \rightleftharpoons O_2 + H_2O$	Acidic	+2.08
	$O_3 + H_2O + 2e^- \rightleftharpoons O_2 + 2OH^-$	Basic	+1.24
Chlorine	$Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-$	–	+1.36
Hypochlorite	$HClO + H^+ + 2e^- \rightleftharpoons Cl^- + H_2O$	Acidic	+1.48
	$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	Basic	+0.84
Chlorine dioxide	$ClO_{2(aq.)} + e^- \rightleftharpoons ClO_2^-$	–	+0.95

biological or other treatment processes. Chlorine rapidly penetrates and kills the bacterial cells. Table 1 shows redox potentials of some of the most important oxidants used in water remediation.

Remediation of heavy metals

Heavy metal contamination of groundwater mainly originates from anthropogenic sources or from natural soil source and is a major concern of public health. Ionic species of these metals in their most stable oxidation state are most toxic, in which they can react with the biomolecules of body to form very stable biotoxic compounds which are difficult to dissociate. Heavy metal poisoning can result from drinking water contamination (e.g., Pb pipes, industrial and consumer wastes) intake via the food chain or high ambient air concentration near emission sources (Lenntech 2004). Redox conditions help in stabilizing the pollutants in less mobile or toxic form, which is the base of various technologies used in heavy metal remediation. Redox reactions can mobilize or immobilize metals, depending on the particular metal species and microenvironments (Violante et al. 2010). Mobility and the toxicity of many elements, such as chromium, selenium, cobalt, lead, arsenic, nickel and copper, depend on their oxidation states which in turn are controlled by the redox reactions. Reduction of soluble Cr(VI) to sparingly soluble Cr(III) decreases mobility, while the reduction of Hg(II) into the volatile Hg(0) increases mobility.

In general, all the arsenic removal technologies are effective for the removal of As(V) and not As(III) which is predominately noncharged, more toxic and has high mobility below pH 9.2. So it is necessary to oxidize As(III) into As(V) (Lescano et al. 2011) before its final removal by using other removal processes such as coagulation, adsorption or ion exchange. As(III) can be converted to As(V) by HClO (Vasudevan et al. 2006) and also by $K_3Fe(CN)_6$ (Tandon and Singh 2011), using air, pure oxygen and ozone (Kim and Nriagu 2000). Tandon et al. (2013a) reported new oxidative route for transformation of As(III) to As(V) by Na_2FeO_4 and its subsequent removal from contaminated water. The other heavy metal which can be subjected to oxidation is selenium. Selenite [Se(IV)] is more mobile, toxic and readily transported in groundwater (Parida et al. 1997) than selenate [Se(VI)]. In view of this, a strict drinking water standard of 10 ppb was proposed for Se by WHO (2006).

Remediation of inorganic pollutants

Industrial effluents generated by metallurgical operations generally contain cyanide (CN^-) which is a toxic species. Cyanides have strong affinity for metals and therefore frequently used for metal finishing and treatment and as a lixiviant for metal leaching, particularly gold. Although safe, these technologies require safeguards to prevent accidental spills from contaminating soils and groundwaters. Various methods of cyanide remediation have been reviewed, and the reaction mechanisms have been proposed. Metabolic conversion of cyanide to cyanate, OCN^- that is less toxic than cyanide, is the predominant mechanism of biooxidation (Young and Jordan 1995; Smith and Mudder 1991; Ingvorgsen et al. 1991).

$$CN^- + 1/2O_2(aq.) \rightarrow OCN^- \tag{4}$$

In addition to cyanide, thiocyanate also may be removed by biooxidation.

$$SCN^- + 3H_2O + 2O_2(aq.) \rightarrow SO_4^{2-} + NH_4^+ + HCO_3^- + H^+ \tag{5}$$

Ammonium ion produced in the above reactions is also considered toxic and must also be treated prior to discharge, usually by nitrification or denitrification processes

Table 2 Oxidation products of sulfur- and nitrogen-containing pollutants by Iron(VI)

Pollutants	Oxidative products	Fe(VI): pollutants (stoichiometric ratio)	Rate constants (M^{-1} s^{-1}) at 25 °C
Cyanide	OCN^-, NO_2^-	1:1	5.00×10^1 (pH = 10.1)
Thiourea	NH_2CONH_2, SO_4^{2-}	8:3	2.00×10^2 (pH = 10.1)
Thiocyanate	OCN^-, NO_2^-, SO_4^{2-}	4:1	1.18×10^0 (pH = 10.1)
Hydrogen sulfide	SO_4^{2-}	8:3	2.95×10^3 (pH = 11.0)

(US EPA 1986a, b). Sharma et al. (2005, and references cited in) reported the kinetics and stoichiometric study of oxidation of sulfur- and nitrogen-containing pollutants, i.e., cyanide, thiourea, thiocyanate and hydrogen sulfide by iron ferrate(VI), into nontoxic/less toxic by-products (Table 2). The reactions of ferrate(VI) with pollutants were found to be first order for each reactant.

Remediation of organic pollutants

Organic contaminants in drinking water generally come from various sources such as energy production (petroleum hydrocarbons), agriculture (pesticides), chemical industry (chlorinated solvents), or weapons' production and use (explosives) (Schwarzenbach et al. 2003). Apart from these in new circumstances, other contaminants from pharmaceuticals, personal care products and steroid hormones have also started polluting the environment (Richardson 2009). Redox processes significantly affect the fate and magnitude of organic pollutants. Various metal oxides such as manganese and iron oxides in soils are reactive surfaces that play an important role in affecting the toxicity, fate and transport of organic contaminants via redox reactions (Zhang et al. 2008). A number of pharmaceuticals such as antibiotics, fibrate lipid regulators and metabolites, antipyretics and nonsteroidal anti-inflammatory drugs, anticonvulsants and anti-anxiety agents and beta blockers recently have been detected globally in surface water and in drinking water. Their presence shows inefficiency of the traditional techniques of wastewater treatment. Oxidative transformation/detoxification of these pharmaceuticals during water treatment with selective oxidants shows most feasible approach for water remediation (Sharma 2008; Huber et al. 2005; Khetan and Collins 2007; Deborde and Gunten 2008; Sharma and Sohn 2012). Oxidants can selectively oxidize pharmaceuticals to readily biodegradable and less toxic compounds. In many remediation processes, oxidants such as Cl_2, HOCl, ClO_2, O_3 and Fe(VI) are frequently used for oxidative treatments of organic pollutants because of their high reduction potentials (Dodd et al. 2006; Ikehata et al. 2006; Esplugas et al. 2007; Sharma 2007). Remediation of contaminated water by oxidation destroys biological effects of pharmaceuticals along with the disappearance of the parent compound. In the absence of full doses of oxidants, complete mineralization is not obtained and pharmaceuticals are only partially transformed as only the selective groups responsible for their effect are oxidized (Huber et al. 2005).

Remediation of microorganisms

Various oxidants such as ozone, chlorine and chloramines are used as disinfectants in water treatment. However, formation of a wide range of by-products and the dependence of percent removal on pH and existing level of chlorine and bromine restrict their use. Antimicrobial activity of ferrate(VI) has been properly investigated in the last few decades (Jiang et al. 2002; Jiang and Wang 2003). Fe(VI) has proved itself as a powerful disinfectant over a wide range of pH at relatively very low initial concentrations. Moreover, the use of ferrate(VI) as disinfectant does not produce any carcinogenic/mutagenic by-products (DeLuca et al. 1983). Fe(VI) has been successfully used in inactivating the microorganisms such as bacteria, viruses, algae, microcystins and biofilm control (Sharma et al. 2005). Fe(VI) mainly inactivates the microorganisms by oxidative disruption of cell membrane and cell components (Basu et al. 1987). Recently, several natural and engineered nanomaterials have been shown to have strong antimicrobial properties, including chitosan (Qi et al. 2004), silver nanoparticles (nAg) (Morones et al. 2005), photocatalytic TiO_2 (Cho et al. 2005), fullerol (Badireddy et al. 2007), aqueous fullerene nanoparticles (nC60) (Lyon et al. 2006) and carbon nano tubes (CNT) (Kang et al. 2007). Nanoparticles can directly interact with the microbial cells, e.g., interrupting transmembrane electron transfer, disrupting/penetrating the cell envelope, or oxidizing cell components, or produce secondary products (e.g., reactive oxygen species (ROS) or dissolved heavy metal ions) that cause damage.

Reduction and water remediation

Reduction also plays important role in destruction or immobilization of various water contaminants. Manipulation of redox conditions of water can be achieved by mixing of liquid or gaseous reductants, or reduced colloids.

Several soluble reductants such as sulfite, thiosulfate, hydroxylamine and dithionite have been studied on bench scale under anoxic conditions. Dithionite has been found to be most effective. The gaseous reductant that has been tested is hydrogen sulfide, and the colloidal reductants are clay-supported Fe(0) and Fe(II).

Remediation of heavy metals

The reductive transformation of some heavy metals may proceed chemically, for example, Cu(II) reduction to Cu(I) by Fe^{2+} or H_2S and reduction of Cu(II), Ag(II), and Hg(II) to elemental forms by Fe(II)-bearing green rust (Borch et al. 2010). Redox reactions can be used to decrease the toxicity or mobility of metal contaminants by converting them to inactive states. Reduction is most commonly used for this purpose. Microorganisms may directly reduce many highly toxic metals (e.g., Cr, Hg and U) via dissimilation or detoxification pathways. Microbial reduction in certain metals to a lower redox state may result in reduced mobility and toxicity. Such processes may accompany other metal precipitation mechanisms also. Aerobic and anaerobic reduction of Cr(VI) to Cr(III) is widespread in microorganisms (Gadd 2008). Iron-based technologies for remediation of contaminated groundwater and soil are a well-documented field. The ability of iron as Fe(0) and Fe(II) to reduce the redox-sensitive elements has been demonstrated at both laboratory scale and in field tests (Kim et al. 2007; Ludwig et al. 2007). Zero-valent iron nanoparticles were found to be a strong chemical reductant and were able to convert many mobile oxidized oxyanions such as $CrO_4{}^{2-}$ and $TcO_4{}^{-}$ and oxycations, i.e., $UO_2{}^{2+}$ into immobile forms (Blowes et al. 1995).

Remediation of inorganic pollutants

Many researchers have studied the reduction of nitrate by zero-valent iron (ZVI). Choe et al. (2000) reported complete conversion of nitrate into nitrogen gas using nanoscale zero-valent iron, although mass balance data were not shown in their research. The reaction between zero-valent iron (ZVI) and nitrate is a redox reaction which produces all the possible reductive species, i.e., $NH_4{}^{+}$, N_2 and $NO_2{}^{-}$, while ZVI is converted into ferrous ion (Fe^{+2}). Ferrous ion produced during nitrate removal further reacts with ZVI to produce Fe_3O_4 on ZVI surface (Huang and Zhang 2002).

$$4Fe^0 + 10H^+ + NO_3^- \rightarrow NH_4^+ + 4Fe^{2+} + 3H_2O \quad (6)$$

$$Fe^0 + 2H^+ + NO_3^- \rightarrow NO_2^- + Fe^{2+} + H_2O \quad (7)$$

$$5Fe^0 + 12H^+ + 2NO_3^- \rightarrow N_{2(g)} + 5Fe^{2+} + 6H_2O \quad (8)$$

$$NO_3^- + 2.82Fe^0 + 0.75Fe^{2+} + 2.25H_2O \rightarrow NH_4^+ + 1.19Fe_3O_4 + 0.50OH^- \quad (9)$$

Fanning (2000) extensively reviewed the use of different reducing agents such as active metals, ammonia, borohydride, formate and other organic species, hydrogen, hydrazine and hydroxylamine, iron(II) and use of energy sources, such as electrochemical, photochemical and thermal, in chemical reduction of nitrate. The reducing agents used for the purpose at acidic pH are formic acid, iron metal, methanol and the ammonium ion while, at basic pH aluminum, zinc and iron metals, iron(II), ammonia, hydrazine, glucose and hydrogen. Due to their high water solubility, low adsorptive capacity, as well as kinetic inertness, perchlorate ($ClO_4{}^{-}$) can easily be spread widely and be quite persistent in surface water and groundwater systems. High levels of $ClO_4{}^{-}$ interfere with iodide uptake into the thyroid gland. For infants and fetuses, the thyroid has a major role in the development of normal central nervous system and skeletal growth. Since the most likely way for pregnant women and mothers to ingest $ClO_4{}^{-}$ is through contaminated drinking water, the US EPA has set an official reference dose which comes out to a drinking water equivalent level of 24.5 ppb (ITRC 2005). At the low concentrations typically encountered (i.e., <500 mg mL^{-1}), it is difficult to analyze and remediate $ClO_4{}^{-}$. Possible technologies include physical separation (precipitation, anion exchange, reverse osmosis and electrodialysis), chemical and electrochemical reduction, and biological or biochemical reduction. Bioremediation is another practical approach. A number of bacteria that contain nitrate reductases (Payne 1973) are capable of reducing $ClO_4{}^{-}$ (Schilt 1979). Rikken et al. (1996) reported that $ClO_4{}^{-}$ and ClO^{3-} are reduced to chloride by proteobacteria with acetate as a nutrient (reductant) at near-neutral pH. While they did show loss of $ClO_4{}^{-}$ and ClO^{3-}, their mechanisms failed to include contributions from uncatalyzed reactions. $ClO_4{}^{-}$ reduction by Vibrio dechloraticans Cuzensove B-1168 has been patented by Korenkov et al. (1976). V. dechloraticans is nonsporulating, motile and gram-negative. Malmqvist et al. (1994) showed that Ideonella dechloratans can reduce ClO^{3-}, but they did not test for $ClO_4{}^{-}$ reduction. Water contaminated with $ClO_4{}^{-}$ thus can best be dealt with bioremediation and biological or biochemical treatment which is the most economically feasible, fastest and easiest means of dealing with $ClO_4{}^{-}$. It appears that in future biological and biochemical approaches in combination with other technologies will play the greatest role in solving the complex $ClO_4{}^{-}$ problem.

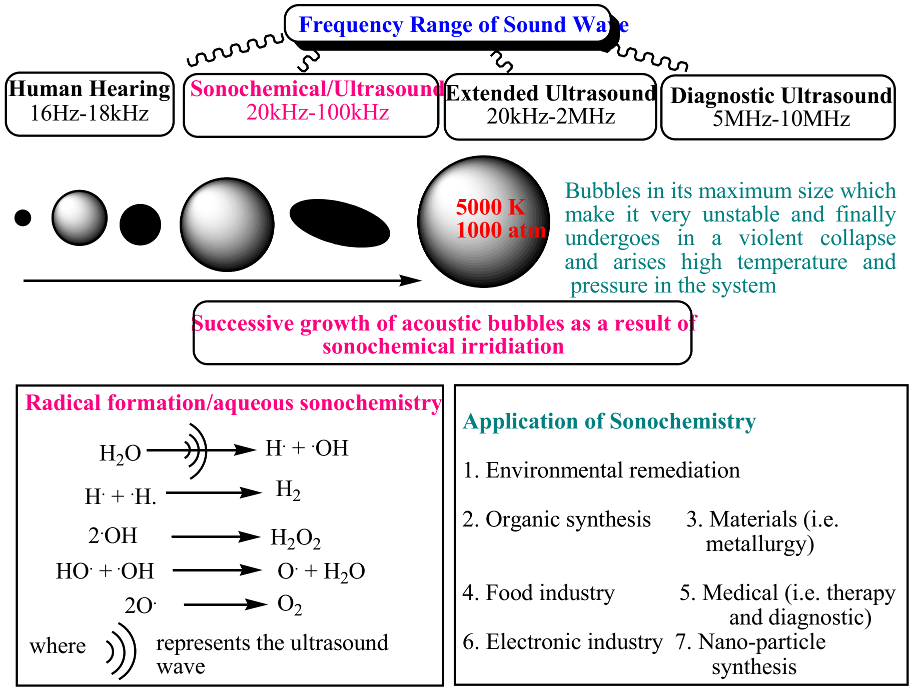


Fig. 2 Schematic representation of details about sonochemistry: ultrasound range, acoustic bubble formation aqueous sonochemistry and application in various fields

Remediation of organic pollutants

It has been shown that instead of pure aqueous Fe^{2+}, Fe(III) oxide phases such as haematite that have reacted with Fe(II) can enhance the rates of transformation of many reducible contaminants (Elsner et al. 2004) such as nitroaromatics (Borch et al. 2005), chlorinated solvents (Amonette et al. 2000), pesticides (Hakala et al. 2007) and disinfectants (Vikesland and Valentine 2002). The enhanced reactivity of Fe(III) oxide surfaces reacted with Fe(II) is poorly understood. In contrast to earlier suggestions of various surface complexation theories for the Fe(II) reactivity (Elsner et al. 2004), it has now been shown that Fe(II) is oxidized to Fe(III) upon adsorption (Handler et al. 2009). Identity of iron oxide surfaces was found to play a significant role in the kinetics of reactions between Fe(II) and monochloramine in the presence of a variety of iron oxide surfaces (Vikesland and Valentine 2002). Finally, a recent study indicated that the Fe(II): Fe(III) stoichiometry of magnetite likely alters the bulk redox properties of the magnetite particle to make reduction of, for instance, nitrobenzene more favorable (Gorski and Scherer 2009).

Water remediation technologies coupled with redox processes

A number of technologies used in water remediation (Caliman et al. 2011) have their advantages and disadvantages. Mobility, toxicity, speciation and biodegradation of various types of water contaminants depend on redox processes. Some of these technologies can be coupled with redox remediation synergistically so that the coupled remediation efficiency is higher than the sum of individual technologies applied individually. Some of the remediation technologies which have close correlation with redox reactions are described below.

Ultrasonication

Ultrasonication remediation process involves use of intense ultrasonic wave energy in liquid media resulting in the formation of microbubbles and generation of high temperature and pressure, which leads to the destruction/oxidation of organic chlorinated compounds directly into nonhazardous end products by the radicals (Collings et al. 2006; Mason 1990a, b). The final products of this process may be hydrogen, carbon dioxide and/or some inorganic compounds, if the reaction is complete. Thus, remediation efficiency of sonochemical methods finally involves redox-based reactions to decontaminate water. Figure 2 gives basic details of sonochemistry in summarized form. Complete destruction of contaminants in soil or water by ultrasonic irradiation can be obtained by the direct oxidation of chemical residues or by desorption and leaching of contaminants from materials (Mason and Lorimer 2002; Mason et al. 2004). Highly stable contaminants which otherwise persist in the environment such as polycyclic aromatic hydrocarbons (PAHs), pesticides, polychlorinated biphenyls (PCBs) and other organochlorides that adsorb to the surface of soil

Table 3 A list of some common contaminants suitable for bioremediation

Contaminants	Major class of contaminants
Atrazine, Carbaryl, Carbofuran, Coumaphos, Diazinon, Glycophosphate, Parathion, Propham, 2,4-D	Pesticides
Benzene, Toluene, Ethylbenzene, Xylene	"BTEX"
Pentachlorophenol	Chlorinated phenol
Trichloroethylene Perchloroethylene	Chlorinated solvents
4-Chlorobiphenyl 4,4-Dichlorobiphenyl	Polychlorinated biphenyls
Naphthalene, Anthracene, Pyrene	Polyaromatic hydrocarbons (PAHs)

particles (Collings et al. 2006) can be dealt easily with ultrasonic treatment.

Bioremediation

Under controlled conditions, biological degradation of organic wastes below the established pollution limits is known as bioremediation (Mueller et al. 1996). Many microorganisms consume certain harmful chemicals converting them into harmless products such as water and carbon dioxide. Microbial digestion of water contaminants mainly based on metabolic processes (redox processes) occurs in microbe cells. In bioremediation, naturally occurring bacteria and fungi or plants are used to detoxify hazardous substances into the less harmful products. Potentially suitable contaminants for bioremediation (Vidali 2001) are given in Table 3.

Electrokinetics

Electrokinetics (EK) is used to separate and extract heavy metals, radionuclides, and organic contaminants from saturated or unsaturated soils, sludges, and sediments. The method uses a low-level direct current as the "cleaning agent," several transport mechanisms (electroosmosis, electromigration and electrophoresis) and electrochemical reactions (electrolysis and electrodeposition) are induced (Acar and Alshawabkeh 1993). Depending on their charge, contaminants, in the aqueous phase or desorbed from the soil surface, are transported toward respective electrodes where they may then be extracted to a recovery system or deposited at the electrode. Surfactants and complexing agents can be used to increase solubility and movement of the contaminant. Reagents may also be introduced at the electrodes to enhance contaminant removal rates. Some of its advantages are close control over the direction of movement of water and dissolved contaminants, retention of contaminants within a confined zone, and low power consumption (Page and Page 2002).

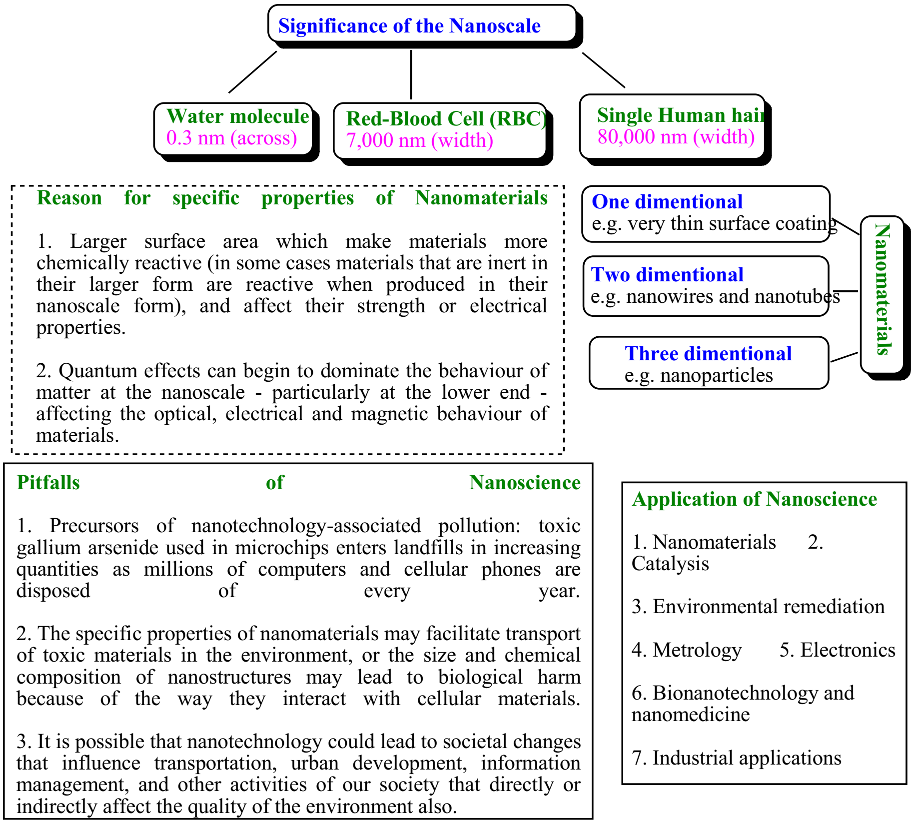
Redox remediation technology mainly oxidation enhances the effectiveness of EK remediation technology used in removal of heavy metals and organic pollutants. Chemical oxidation with EK has been tested by several researchers, namely for phenanthrene-spiked soil with Fenton's reagent (Kim et al. 2006), phenol-spiked kaolin with $KMnO_4$ (Thepsithar and Roberts 2006) and diesel-contaminated soils with H_2O_2 (Tsai et al. 2010).

Nanotechnology for water remediation

Nanoparticles can be highly reactive due to their large surface area to volume ratio and the presence of a greater number of reactive sites. This allows for increased contact with contaminants, thereby resulting in rapid reduction of contaminant concentrations. Modified iron nanoparticles, such as catalyzed and supported nanoparticles, have been synthesized to further enhance the speed and efficiency of remediation (Zhang 2003). Figure 3 gives summarized details about nanoscience.

In addition to the common environmentally relevant electron acceptors, zero-valent iron also readily reacts with a wide variety of redox-amenable contaminants (Tandon et al. 2013b). Matheson and Tratnyek (1994) reported that ZVI in situ acts as three electron donor systems which includes Fe^0, Fe(II) and H_2 for reductive decontamination of water (Scheme 1).

Because of their minute size, nanoparticles may pervade very small spaces in the subsurface and remain suspended in groundwater, which would allow the particles to travel farther than macrosized particles and achieve wider distribution (Tratnyek and Johnson 2006). Research has shown that zero-valent iron nanoparticles (nZVIs) are very effective for the transformation and detoxification of a wide variety of common environmental contaminants such as chlorinated organic solvents, organochlorine pesticides and polychlorinated biphenyls (Zhang 2003). Nanoparticles are traditionally injected under pressure and/or by gravity to the contaminated plume where treatment is needed. However, the transport of nZVI is normally limited by their aggregation and settlement (Jiemvarangkul et al. 2011). The mobility of nZVI will be less than a few meters under almost all conditions, so the possibility of enhancing its transport through EK is very interesting. There is also a lot of potential in the application of nZVI to



Reason for specific properties of Nanomaterials

1. Larger surface area which make materials more chemically reactive (in some cases materials that are inert in their larger form are reactive when produced in their nanoscale form), and affect their strength or electrical properties.

2. Quantum effects can begin to dominate the behaviour of matter at the nanoscale - particularly at the lower end - affecting the optical, electrical and magnetic behaviour of materials.

Pitfalls of Nanoscience

1. Precursors of nanotechnology-associated pollution: toxic gallium arsenide used in microchips enters landfills in increasing quantities as millions of computers and cellular phones are disposed of every year.

2. The specific properties of nanomaterials may facilitate transport of toxic materials in the environment, or the size and chemical composition of nanostructures may lead to biological harm because of the way they interact with cellular materials.

3. It is possible that nanotechnology could lead to societal changes that influence transportation, urban development, information management, and other activities of our society that directly or indirectly affect the quality of the environment also.

Application of Nanoscience

1. Nanomaterials 2. Catalysis

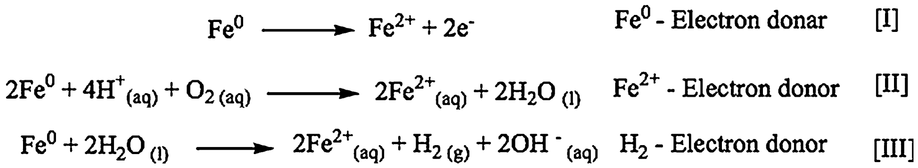
3. Environmental remediation

4. Metrology 5. Electronics

6. Bionanotechnology and nanomedicine

7. Industrial applications

Fig. 3 Nanoscience: summarized introduction, applications and limitations



$$Fe^0 \longrightarrow Fe^{2+} + 2e^- \qquad Fe^0 \text{ - Electron donar} \qquad [I]$$

$$2Fe^0 + 4H^+_{(aq)} + O_{2\,(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \qquad Fe^{2+} \text{ - Electron donor} \qquad [II]$$

$$Fe^0 + 2H_2O_{(l)} \longrightarrow 2Fe^{2+}_{(aq)} + H_{2\,(g)} + 2OH^-_{(aq)} \qquad H_2 \text{ - Electron donor} \qquad [III]$$

Scheme 1 ZVI reduction generated three electron donor species

organochlorines, given their high reactivity and the fact that it effectively dechlorinates these compounds into less toxic and more biodegradable ones (Zhang et al. 2011).

Conclusion

For the sustainability of life on earth, water plays a vital role, and therefore, pollution of water creates an urgent need to remediate it. Main problem with most of the remediation technologies is that removal of one pollutant creates the problem of polluting water by other pollutant which may be generated as an intermediate or the side product. Hence, it is necessary for researchers and decision makers to consider all the factors before implementing any technology for water remediation. The present article throws light on the comparative study of the advantages and disadvantages of various remediation techniques based on redox processes which are currently employed in the remediation of water. It also explores the possibilities of coupling different technologies with redox processes for better efficiency.

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